



Research paper

Heterogeneous oxidation of elemental mercury vapor over RuO₂/rutile TiO₂ catalyst for mercury emissions control

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ABSTRACT

The catalytic oxidation of elemental mercury (Hg(0)) vapor is an effective way to enhance mercury removal from coal-fired power plants. RuO₂ catalyst was found to be an excellent Hg(0) oxidation catalyst. When rutile TiO₂ was used as the catalyst support, RuO₂ formed well dispersed nano-layers due to the very similar crystal structures of RuO₂ and rutile TiO₂, giving higher Hg(0) oxidation activity over anatase TiO₂ support. The RuO₂/rutile TiO₂ catalyst can be used at the tail end section of the selective catalytic reduction (SCR) unit for Hg(0) oxidation. It showed good Hg(0) oxidation performance under sub-bituminous and lignite coal simulated flue gas conditions with low concentration of HCl or HBr gas. The RuO₂/rutile TiO₂ catalyst also showed excellent resistance to SO₂ under bituminous coal simulated flue gas, maintaining higher than 90% Hg(0) oxidation with up to 2,000 ppmv SO₂ present. The oxidized mercury in a form of HgCl₂ has a high solubility in water and can be easily captured by other air pollution control systems such as wet scrubbers in coal-fired power plants.

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1. Introduction

Coal naturally contains small amounts of mercury (around 0.1–0.2 ppm by weight) and they will be released into the flue gas after the combustion [1,2]. It is estimated that around 53 tons of mercury are emitted from coal-fired power plants each year in the United States, accounting for around 50% of emissions from all anthropogenic mercury sources [3]. Mercury has long been recognized as a highly toxic and persistent pollutant. The 1990 Amendments to the Clean Air Act listed mercury as one of the most toxic pollutants among 188 hazardous air pollutants. In 2012, the U.S. EPA finalized the air toxics standards for coal- and oil-fired electric generating units also known as the Mercury Air Toxics Standards (MATS) [4]. Prior to the MATS rule in 2011, EPA finalized the Cross-State Air Pollution Rule (CSAPR), replacing the EPA's earlier Clean Air Interstate Rule (CAIR) from 2005 [5]. CSAPR further reduces NO_x and SO₂ emissions from power plants in 28 states, and as a result, additional installations of flue gas desulfurization (FGD) and NO_x control systems such as a selective catalytic reduction (SCR) unit are expected.

After combustion, mercury is released and exists in three forms in coal-fired power plants flue gas: oxidized mercury (Hg(2+)), particulate mercury (Hg(p)), and elementary mercury (Hg(0)). The first two forms are readily removed with existing air pollution control systems such as fabric filter (FF), electrostatic precipitators (ESP), and wet FGD [6–8]. Hg(0) is most difficult to remove due to its high volatility, low reactivity and low solubility. Currently, sorbent injection (raw or modified activated carbon), halogen salt (e.g. CaBr₂) addition to the boiler and SCR optimization are commercially available mercury emissions control technologies [9]. Because of the vastly different coal properties and power plant configurations, there is no universal mercury control solution that fits all scenarios, and combinations of control methods are often needed. Activated carbon injection is the most well-studied and mature technology, but the cost is high. The U.S. Department of Energy estimates that the costs for sorbent injection to achieve 90 percent removal are estimated to be between \$25,000 and \$70,000 per pound of mercury removed [10]. Also, activated carbon sorption capacity is significantly reduced under high sulfur coal conditions [11]. Due to the increasing number of FGD units resulted from recent EPA rules, oxidizing elemental mercury using SCR or other catalysts, followed by oxidized mercury capture in wet FGD is a viable option. Noble metal-based catalysts such as gold, platinum and palladium have been studied as Hg(0) oxidation catalysts [12,13]. Various metal oxide-based Hg(0) oxidation

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catalysts, SCR and modified SCR catalysts have also been studied for Hg(0) oxidation [14–22]. Due to the oxygen storing and releasing property of CeO₂, its application in Hg(0) oxidation and adsorption in flue gas has been studied in recent years. Nanostructured CeO₂-MnO_x catalyst and CeO₂-based solid solutions showed good Hg(0) removal performance from increased oxygen vacancies and catalytic activity [23,24]. CeO₂-TiO₂ and CeO₂ modified MnO_x-TiO₂ were reported to have Hg(0) adsorption capability [25,26]. CeO₂ was also reported to have a promotional effect for Hg(0) oxidation in a modified SCR catalyst [27]. But, most of them only showed limited Hg(0) oxidation performances at low HCl concentrations of typical flue gases from lignite and sub-bituminous coals. Also, these catalysts are susceptible to SO₂ and NH₃ inhibition and showed degraded performances under high sulfur bituminous coal flue gas conditions (e.g., 2,000 ppmv SO₂). For low rank sub-bituminous and lignite coals with low chlorine (typically with HCl <10 ppmv in the flue gas), additional halogen is usually needed to achieve satisfactory Hg(0) oxidation. Currently, halogen salts such as CaCl₂ or CaBr₂ injection to the boiler to enhance Hg(0) oxidation is one of the most widely used methods [28]. In the absence of any catalyst (either SCR or Hg(0) oxidation catalyst), high injection rate of the halogen salts is required, and it was reported to cause corrosion problems especially in the air-preheater [29,30]. A combination of halogen salts addition and Hg(0) oxidation catalysts could be an economical and feasible solution [31].

Recently, RuO₂-based catalysts were developed for the Deacon reaction for the oxidation of HCl by O₂ to produce Cl₂ [32,33]. It was also found that many Deacon reaction catalysts can also catalyze the Hg(0) oxidation reaction by utilizing HCl gas [17]. In our previous study, oxidized mercury species obtained from the RuO₂/rutile TiO₂ catalyst were analyzed using X-ray Absorption Near-Edge Structure (XANES) spectroscopy [34]. A major focus of the study was to identify and quantify the oxidized mercury species generated as a result of the reaction of Hg(0) vapor over the catalyst under different simulated flue gas conditions. In the presence of HCl or HBr gas with O₂ gas, HgCl₂ or HgBr₂ was found to be a major oxidized mercury species. HgCl₂ and HgBr₂ have high solubility in water, and can be easily scrubbed by wet FGD scrubbers in coal-fired power plants. In this study, the performances of the RuO₂/rutile TiO₂ catalyst were investigated in terms of different TiO₂ phases, synthesis methods and gas and temperature conditions.

2. Experimental

2.1. Catalyst synthesis

RuO₂/TiO₂ catalysts were synthesized using RuCl₃ (Sigma-Aldrich) as the precursor. Commercial anatase- and rutile-phase TiO₂ were obtained from Cristal Co. and Sakai Chemical, respectively. Three synthesis methods were used for RuO₂/TiO₂ catalysts, and the procedures are summarized below.

Wetness incipient (WI) method: RuCl₃ was dissolved in a small amount of water (around 0.9 mL per gram of TiO₂) and the solution was added to dry TiO₂ powder. After thorough mixing, the catalyst was dried at room temperature for 12 h and calcined at 400 °C in air for 3 h.

Deposition-precipitation (DP) method: TiO₂ powder was added to water (25 mL water per gram of TiO₂ powder) under vigorous stirring. Then RuCl₃ was added and the slurry was heated to 45 °C. A 1 M Na₂CO₃ solution was added dropwise until pH > 10 to precipitate all RuCl₃ [35,36]. The catalyst was then filtered, washed thoroughly, dried at room temperature for 12 h and calcined at 400 °C in air for 3 h.

Strong electrostatic adsorption (SEA) method: TiO₂ powder was added to water (25 mL water per gram of TiO₂ powder) under vig-

orous stirring and an ammonium hydroxide solution was added until pH reached 11.5. RuCl₃ was then added and stirred for 3 h [37]. This method utilizes electrostatic charges for adsorption of active metals onto substrate. The point of zero charge (PZC) for TiO₂ in the aqueous phase is around 6. When the pH of a solution is greater than that the PZC (i.e. ~6), TiO₂ surface is negatively charged. Ru(NH₃)₆³⁺ formed from RuCl₃ and ammonium hydroxide is positively charged and adsorbs onto the TiO₂ surface. The catalyst was then filtered, washed thoroughly, dried at room temperature for 12 h and calcined at 400 °C in air for 3 h.

SCR catalyst with 1 wt% V₂O₅ loading was synthesized by following a procedure below: 12 g of anatase TiO₂ powder (DT-58, Cristal, containing 9.1 wt% tungsten and 10.5 wt% silica), 0.3 g of methylcellulose (Sigma-Aldrich) and 0.24 g of glass fiber (Fibre Glast) were dry mixed for 10 min. 0.138 g of NH₄VO₃ (Sigma-Aldrich) dissolved in 11 mL of 1 M oxalic acid (Sigma-Aldrich) was added to the above powders and the dough was kneaded for 10 min for uniform mixing. All the catalysts were extruded into 1 mm (diameter) × 5 mm (length) cylindrical pellets, and were dried in air at room temperature, followed by calcination at 500 °C in air for 3 h.

2.2. Characterization

The BET surface area, pore volume and pore diameter were measured by an accelerated surface area and porosimetry system (ASAP 2020, Micromeritics). The high-resolution transmission electron microscopy (HR-TEM) experiments were conducted using JEOL 2010F equipped with a field emission gun operating at 200 keV with a point-to-point resolution of 0.19 nm. Energy-dispersive X-ray spectroscopy was conducted using the same instrument with an Oxford INCA EDX detector. The X-ray diffraction (XRD) measurement was carried out with an X'Pert Pro MPD X-ray diffractometer under Cu K α radiation (wavelength = 1.5406 Å). The powdered samples were loaded in an aluminum holder with a depth of 1 mm. The scanning range was from 10 to 60° (2 θ) with a step size of 0.02° and a time step of 0.5 s. Ruthenium K edge (22,117 eV) X-ray absorption fine structure (XAFS) spectra were collected using the 9-BM-B beamline (Sector 9) at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL, Chicago, IL). A Si (111) monochromator was used, with energy resolution ($\Delta E/E$) of approximately 1.4×10^{-4} . Energy calibration was monitored by measuring the absorption through a reference ruthenium foil simultaneously with the absorption through the samples. Samples were loaded onto Teflon holder between two layers of Kapton tapes and measured in transmission mode. A RuO₂ standard was obtained from Sigma-Aldrich. A spent RuO₂/rutile TiO₂ catalyst sample treated after 48 h of Hg(0) oxidation under a simulated flue gas (containing 15 ppbv Hg(0), 10 ppmv HCl, 5 ppmv NH₃, 5 ppmv NO, 200 ppmv SO₂, 3%(v) O₂, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂) at 350 °C was also examined for XRD and XAFS analyses. At least five scans were collected for each sample in order to improve the signal-to-noise ratio. XAFS data collected were analyzed using the Athena software package [38].

2.3. Performance tests

The performances of RuO₂/TiO₂ catalysts were tested using a fixed-bed reactor system. A schematic of the apparatus is shown in Fig. 1. Elemental mercury (Hg(0)) vapor was generated using a permeation oven (Dynacalibrator, VICI Metronics) using N₂ as a carrier gas and the inlet Hg(0) vapor concentration was 10–15 ppbv. Water vapor was generated using a bubbler. All the other simulated flue gas components were prepared from compressed gas cylinders (Wright Brothers, Inc.) and the concentrations were controlled by mass flow controllers. The catalysts with ruthenium metal loading of 0.2–1 wt% (in terms of Ru) were used for the performance tests.

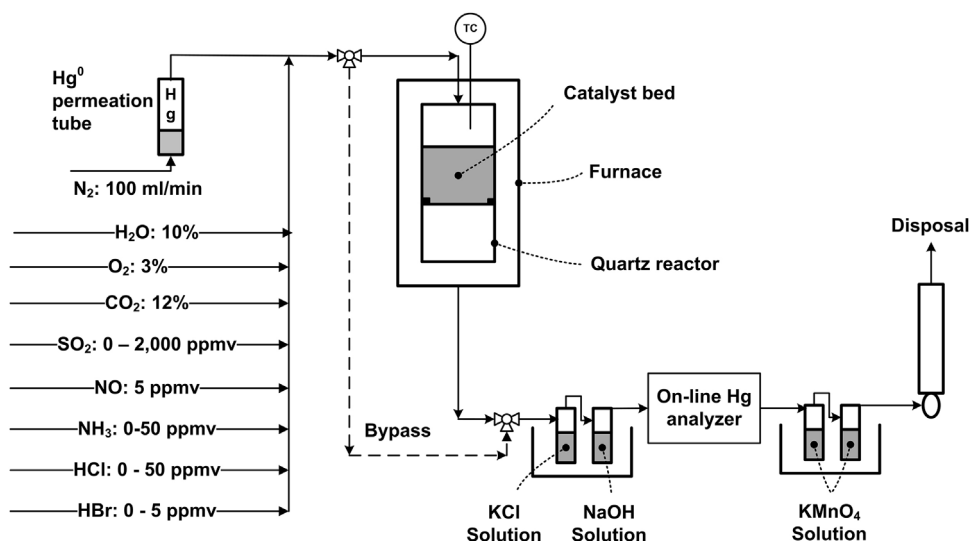


Fig. 1. A schematic of the experimental set-up for the catalysts performance test.

The catalysts in the form of extruded pellets (1 mm × 5 mm (D × L)) were placed inside a vertically mounted quartz reactor with a diameter of 16 mm and the temperature was maintained at 350 °C in a tubular furnace. For performance tests under simulated flue gas conditions, 1.7 g of catalysts were used and the catalyst bed height was around 15 mm. The temperature was chosen to approximate the temperature at the tail end of the SCR unit at coal-fired power plants. The total flow rate of the simulated flue gas was 1 L/min with a gas hourly space velocity 40,000 h^{−1} (about 10 times higher than typical commercial SCR units). It was confirmed that Hg(0) oxidation under the simulated flue gas conditions was negligible in the absence of the catalysts. Each performance test was conducted for 6–24 h after making sure that the system was stabilized. The Hg(0) oxidation efficiency and oxidation rate were calculated by measuring the concentrations across the reactor bed using the following Eqs. (1) and (2):

$$\text{Hg(0) oxidation efficiency} = \frac{\text{Hg(0)}_{\text{in}} - \text{Hg(0)}_{\text{out}}}{\text{Hg(0)}_{\text{in}}} \times 100\% \quad (1)$$

$$\text{Hg(0) oxidation rate} = \frac{\text{Hg(0)}_{\text{in}} - \text{Hg(0)}_{\text{out}}}{\text{time}} \quad (2)$$

SO₃ generated from the catalyst under a simulated flue gas containing high SO₂ concentration was measured using U.S. EPA Method 8 [39]. Two impinger solutions containing 80%(v) isopropanol in water and 3%(v) H₂O₂ in water in series were used to capture SO₃ and SO₂, respectively. Then both fractions were measured separately by the barium-thorin titration method.

3. Results and discussion

3.1. Catalysts characterization

3.1.1. TEM

In this study, two types of TiO₂ support (anatase and rutile) and three synthesis methods (WI, DP, SEA) were used. The TEM images of these RuO₂/TiO₂ catalysts with 1%(wt) Ru loading were taken to obtain the information on the morphology of the metal oxides. When anatase TiO₂ was used, RuO₂ formed large aggregates ranging from 50 to 100 nm for all three synthesis methods as shown in Fig. 2-b, 2-c and 2-d. RuO₂ particles were much bigger than anatase TiO₂ particles and the metal dispersion was poor. EDX indicated that RuO₂ mainly existed as large aggregates and there was only a very small amount present on the anatase TiO₂ surface. The mor-

Table 1

BET surface area, pore volume and average pore diameter measurements for synthesized RuO₂/rutile TiO₂ and SCR catalysts.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (Å)
Rutile TiO ₂	72	0.38	202
0.2% Ru loading	69	0.31	194
0.5% Ru loading	66	0.28	184
1% Ru loading	64	0.28	186
Synthesized SCR	95	0.29	126
Commercial SCR [36–39]	61–120	0.17–0.29	103–151

phology of RuO₂ changed significantly when rutile TiO₂ was used as a support. Under low resolution TEM, no RuO₂ particle could be found from all the three different synthesis methods. However, EDX proved that RuO₂ was present on the surface. Fig. 2-e and 2-f are rutile TiO₂ and RuO₂/rutile TiO₂ (prepared by WI) samples, respectively. The lighter spots on the TiO₂ surface are holes and pores. In order to confirm the morphology of RuO₂, the catalysts were also examined by high resolution TEM. Rutile TiO₂ itself had clean surfaces (Fig. 2-g). After doping with ruthenium, it was found that RuO₂ formed a thin uniform coating on rutile TiO₂ surface with a thickness of 1–2 nm as shown in Fig. 2-h. No noticeable difference on RuO₂ morphology was observed among the three different synthesis methods.

For RuO₂ as a Deacon catalyst, Seki also reported the formation of a nano-sized layer of RuO₂ crystals on rutile TiO₂ [32]. Xiang et al. observed the transformation from RuO₂ particles to epitaxial layer during Deacon reaction [40]. Both RuO₂ and rutile TiO₂ have the same body-centered tetragonal structure with very similar lattice constants: RuO₂ with a = b = 0.46 nm, c = 0.30 nm and rutile TiO₂ with a = b = 0.45 nm, c = 0.31 nm. This similarity makes it easier for RuO₂ to deposit onto rutile TiO₂ surface and to form highly dispersed nano-layers [40,41]. These results suggest that lattice matching between RuO₂ and rutile TiO₂ be a stronger driving force for the dispersion of RuO₂ than the effects of different catalyst synthesis methods.

3.1.2. BET

The BET surface area, pore volume and average pore diameter of RuO₂/rutile TiO₂-WI catalysts with different metal loadings and synthesized SCR catalyst were measured and listed in Table 1. The BET surface area, pore volume and average pore diameter decreased from 72 to 64 m²/g, 0.38–0.28 cm³/g and 202–186 Å, respectively,

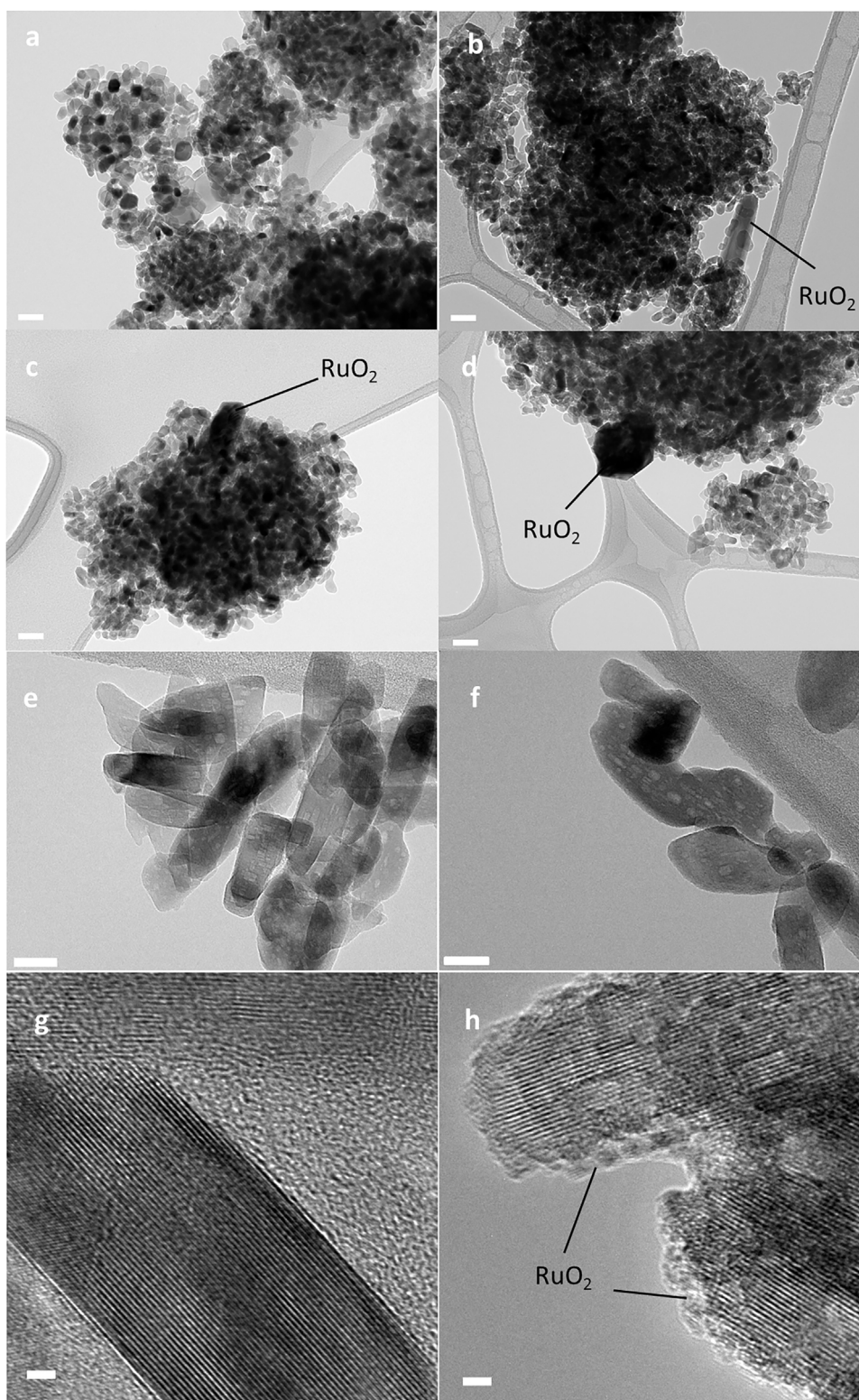


Fig. 2. TEM images of the $\text{RuO}_2/\text{TiO}_2$ catalysts with different supports and synthesis methods. a: anatase TiO_2 ; b: $\text{RuO}_2/\text{anatase TiO}_2\text{-WI}$; c: $\text{RuO}_2/\text{anatase TiO}_2\text{-DP}$; d: $\text{RuO}_2/\text{anatase TiO}_2\text{-SEA}$; e: rutile TiO_2 ; f: $\text{RuO}_2/\text{rutile TiO}_2\text{-WI}$; g: HR-TEM of rutile TiO_2 ; h: HR-TEM of $\text{RuO}_2/\text{rutile TiO}_2\text{-WI}$. Scale bars: a–d=50 nm; e–f=20 nm; g–h=2 nm.

as the ruthenium loading increased to 1 wt%. The impregnation of ruthenium onto rutile TiO_2 did not significantly decrease surface area or block the pores. For the synthesized SCR catalyst, the anatase TiO_2 support had a higher BET surface area than rutile TiO_2 , and the values measured were within a range of typical commercial SCR catalysts [42–45].

3.1.3. XRD

Both $\text{RuO}_2/\text{anatase TiO}_2\text{-WI}$ and $\text{RuO}_2/\text{rutile TiO}_2\text{-WI}$ catalysts were examined by XRD and the patterns are shown in Fig. 3. Other synthesis methods (DP and SEA) showed the same results as the WI method. The $\text{RuO}_2/\text{anatase TiO}_2$ catalyst showed two additional RuO_2 peaks at $2\theta = 28.0^\circ$ and 35.1° compared to pristine anatase

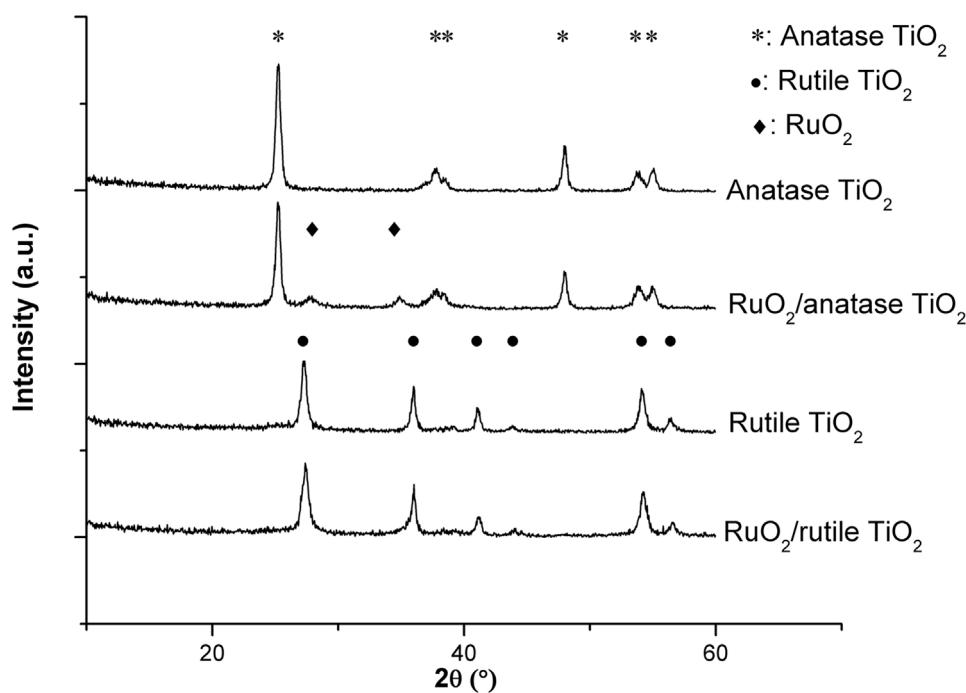


Fig. 3. XRD patterns of different TiO_2 and $\text{RuO}_2/\text{TiO}_2$ -WI catalysts.

TiO_2 . However, when rutile TiO_2 was used as a support, no RuO_2 could be detected. This result was consistent with the information obtained from the TEM results. On anatase TiO_2 , the RuO_2 crystal formation could be easily detected by XRD, while the nano-layers of RuO_2 were formed on rutile TiO_2 . For nano-structures, the local atom arrangements lack long-range 3-D periodicity that typical crystals have, making XRD nonideal for analyzing nanomaterials [46]. Therefore, an alternative characterization technique was needed to identify the ruthenium species on rutile TiO_2 .

3.1.4. XAFS

XAFS can give structural information of materials not affected by the state or morphology of the sample. Since XRD was unable to detect the RuO_2 nano-layers formed on rutile TiO_2 , XAFS was used to confirm the speciation of ruthenium. RuO_2 catalysts supported on rutile TiO_2 were used for the analysis. Ruthenium K edge (22,117 eV) XAFS spectra for the $\text{RuO}_2/\text{rutile TiO}_2$ catalyst were collected. Since XAFS is an element-specific characterization technique, TiO_2 in the catalyst does not interfere with the ruthenium measurement. The Fourier transformed spectra $\chi(R)$ are shown in Fig. 4. $\text{RuO}_2/\text{rutile TiO}_2$ catalysts with different synthesis methods showed the same result and only the result obtained from WI is shown here. Compared with a RuO_2 standard, a fresh $\text{RuO}_2/\text{rutile TiO}_2$ catalyst showed the same structure. The first major peak at around 1.5 Å is from a ruthenium atom and the neighboring oxygen atoms, and the second major peak at around 3.1 Å is from a center ruthenium atom and the neighboring ruthenium atoms. The spectra are similar to those reported in other studies [47,48]. The spectrum of the spent catalyst did not show any change, indicating that RuO_2 was structurally stable under the simulated flue gas conditions.

3.2. $\text{Hg}(0)$ oxidation performances

3.2.1. Effects of TiO_2 support and metal loading

The above catalyst characterization results showed major differences in morphology and dispersion of RuO_2 on anatase and rutile TiO_2 supports. Therefore, $\text{Hg}(0)$ oxidation performances of 1 wt%

RuO_2 catalysts with different TiO_2 supports and synthesis methods were evaluated and the results are shown in Fig. 5. Although the surface area of rutile TiO_2 is slightly lower than anatase TiO_2 under the same conditions, the $\text{Hg}(0)$ oxidation performances of $\text{RuO}_2/\text{rutile TiO}_2$ catalysts were around 70% higher than those of $\text{RuO}_2/\text{anatase TiO}_2$ catalysts on average. When RuO_2 was used as a Deacon catalyst for HCl oxidation, higher catalytic activity of RuO_2 was reported over rutile TiO_2 [32]. However, it is important to note that the different synthesis methods did not result in significant performance differences. These results are consistent with TEM images. The higher dispersion of RuO_2 over rutile TiO_2 due to lattice matching of these two very similar structures very likely leads to higher catalytic activity. Therefore, rutile TiO_2 was chosen as a preferred substrate in this study, and WI was also selected as a preferred synthesis method because of its simplicity.

As a precious metal, a ruthenium loading on catalyst support should be optimized for the maximum utilization of the active metal. Therefore, the $\text{RuO}_2/\text{rutile TiO}_2$ catalyst with different ruthenium loadings (0.2, 0.5 and 1 wt%) were compared (Fig. 6). In terms of the reaction rate of $\text{Hg}(0)$ oxidized per mole of ruthenium used (i.e. turnover frequency), 0.5 wt% Ru loading gave the highest ruthenium utilization efficiency. The determination of RuO_2 on TiO_2 support using a chemisorption method has an inherent difficulty. It is well reported in the literature that the reduced form of RuO_2 (i.e. Ru) becomes mobile and agglomerates on the TiO_2 surface during the reduction step in chemisorption. This phenomena was reported by Komaya et al., and the attempts to eliminate the agglomeration by using different reduction conditions were not successful [49]. In this study, the determination of RuO_2 dispersion over rutile the TiO_2 phase was also attempted, but was not successful. Therefore, mass was used as a basis for the Ru loading instead of dispersion.

3.2.2. Effects of temperature

When RuO_2 was used as a Deacon catalyst, the activity was reported to be highest at around 400 °C [41]. This $\text{RuO}_2/\text{rutile TiO}_2$ $\text{Hg}(0)$ oxidation catalyst can be located between the economizer and air preheater at coal-fired power plants. For power plants with a SCR unit, the catalyst can be located inside the SCR unit, or it can

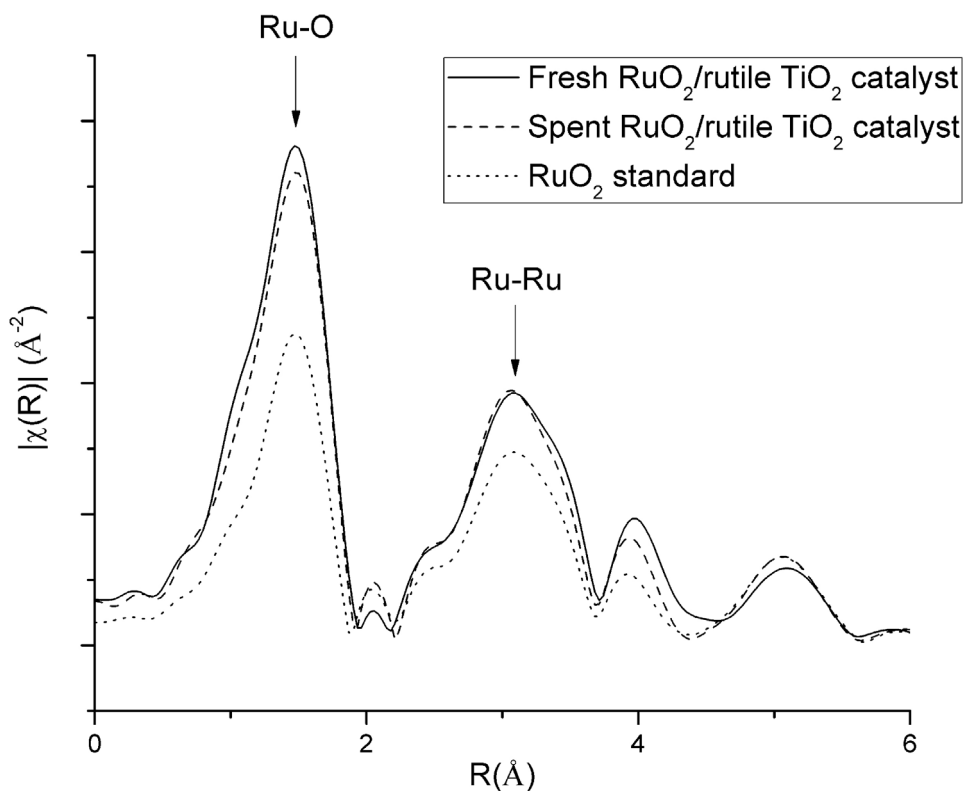


Fig. 4. Fourier transformed Ru XAFS spectra ($|\chi(R)|$) for fresh $\text{RuO}_2/\text{rutile TiO}_2$.WI, spent $\text{RuO}_2/\text{rutile TiO}_2$.WI and RuO_2 standard.

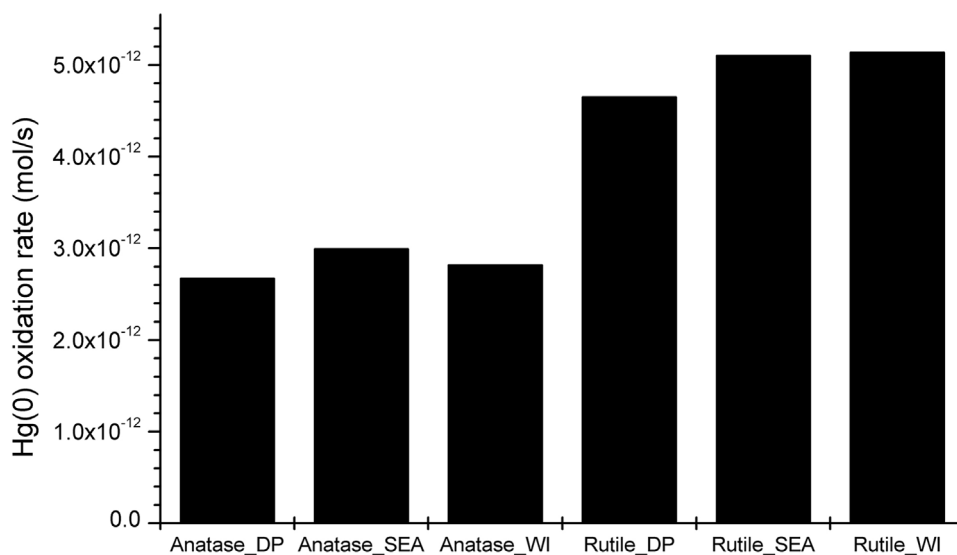


Fig. 5. $\text{Hg}(0)$ oxidation activities of 1 wt% $\text{RuO}_2/\text{TiO}_2$ catalysts with different TiO_2 supports and synthesis methods. Conditions: 10 ppbv $\text{Hg}(0)$, 10 ppmv HCl , 3%(v) O_2 , and balance N_2 at $T = 350^\circ\text{C}$.

be a stand-alone unit before or after the SCR unit. $300\text{--}400^\circ\text{C}$ is an optimal temperature window for typical SCR catalysts when the boilers are at a full load [50]. The $\text{RuO}_2/\text{rutile TiO}_2$ $\text{Hg}(0)$ oxidation catalyst can also utilize the same temperature window. The $\text{Hg}(0)$ oxidation performances of $\text{RuO}_2/\text{rutile TiO}_2$ catalyst at temperatures between 300 and 400°C were evaluated as shown in Fig. 7. The results indicated that $\text{RuO}_2/\text{rutile TiO}_2$ catalyst prefers higher temperature within the temperature window for $\text{Hg}(0)$ oxidation.

3.2.3. $\text{Hg}(0)$ oxidation under simulated flue gases

For coal-fired power plants with SCR units for NO_x removal, NH_3 as a reductant is injected into the front end of the SCR units. As the de- NO_x reaction proceeds, NH_3 concentration decreases along the SCR unit, and an NH_3 slip at the tail end is usually controlled at <2 ppmv for commercial SCR catalysts [51]. The effect of NH_3 gas on $\text{Hg}(0)$ oxidation is shown in Fig. 8. NH_3 has a strong inhibition effect on $\text{Hg}(0)$ oxidation over $\text{RuO}_2/\text{rutile TiO}_2$ catalyst. The catalyst lost almost all its $\text{Hg}(0)$ oxidation capability when NH_3 concentration

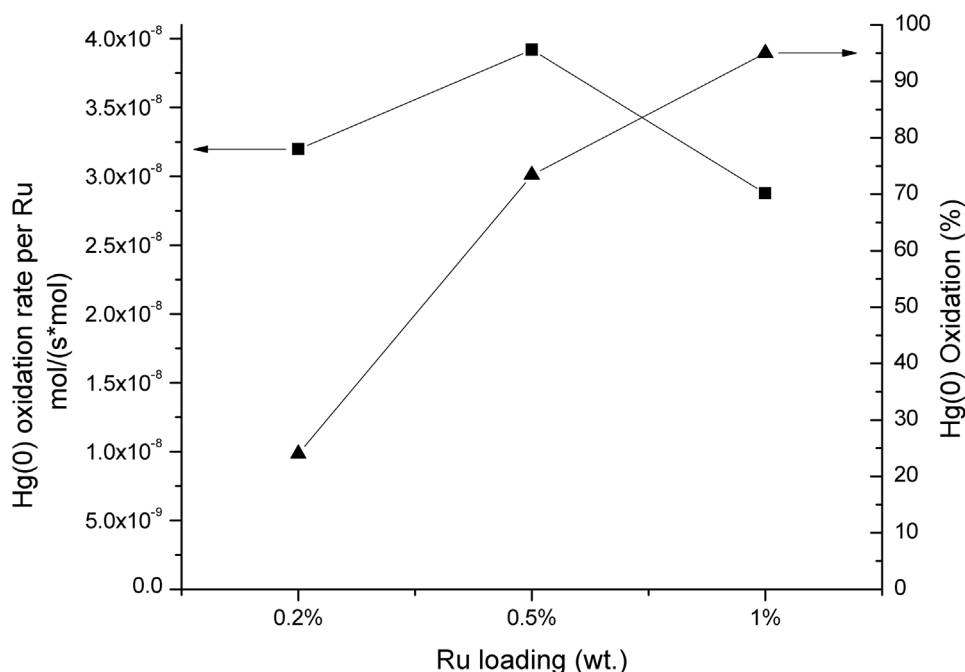


Fig. 6. Effect of metal loadings on the utilization efficiency of ruthenium on rutile TiO_2 (WI method). Conditions: 10 ppbv Hg(0), 10 ppmv HCl, 3%(v) O_2 , and balance N_2 at $T = 350^\circ\text{C}$.

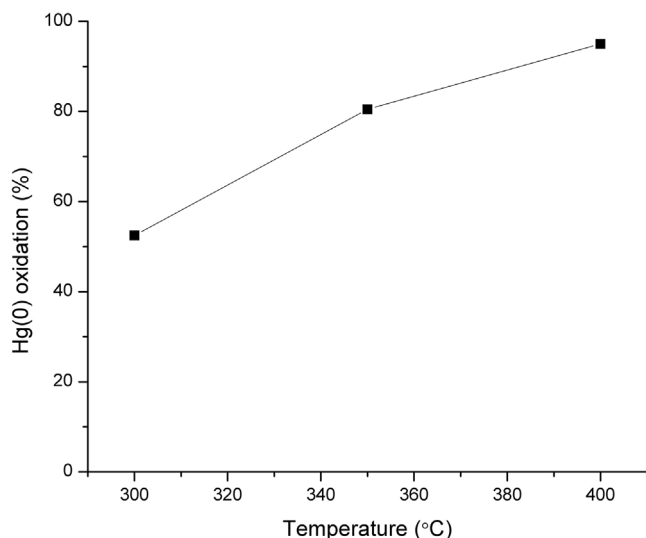


Fig. 7. Effect of temperature on the 1 wt% RuO_2 /rutile TiO_2 -WI catalyst activity. Conditions: 10 ppbv Hg(0), 5 ppmv HCl, 3%(v) O_2 , and balance N_2 .

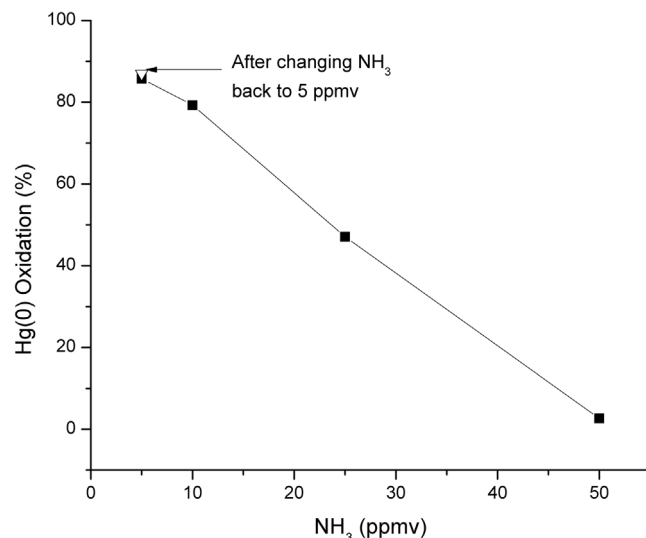


Fig. 8. Effect NH_3 concentrations on Hg(0) oxidation performances of 1 wt% RuO_2 /rutile TiO_2 -WI catalyst under simulated flue gas. Conditions: 15 ppbv Hg(0), 10 ppmv HCl, 5 ppmv NO, 200 ppmv SO_2 , 3%(v) O_2 , 10%(v) H_2O , 12%(v) CO_2 balanced with N_2 at 350°C .

was increased to 50 ppmv. When the 50 ppmv NH_3 was lowered back to 5 ppmv, Hg(0) oxidation was fully recovered. This corroborates that the adverse effect of NH_3 is most likely derived from competitive adsorption with HCl onto active catalytic sites and not catalyst poisoning. Due to this limitation, the RuO_2 /rutile TiO_2 catalyst is not suitable for being located at the front end of a SCR unit. Installing at the tail end of a SCR unit, after the SCR unit, or for power plants without the SCR unit are possible options.

A SO_2 concentration in a coal combustion flue gas greatly varies in terms of different types of coals with different sulfur contents. Generally, lignite and sub-bituminous coals have low SO_2 (a few hundred ppmv in the flue gases) while bituminous coal has high SO_2 (up to ~2,000 ppmv in the flue gas). The Hg(0) oxidation performances under different SO_2 concentrations are shown in Fig. 9. It should be noted that these tests were carried out with only 10 ppmv

HCl just to demonstrate the effect of SO_2 under extreme conditions. For bituminous coal flue gas with high SO_2 concentration, the HCl concentration is also much higher (e.g., ~50–200 ppmv). Under such high HCl concentrations, the resistance of Hg(0) oxidation to SO_2 is much lower as reported in our previous study [34]. In general, the RuO_2 /rutile TiO_2 catalyst has higher resistance to SO_2 compared with other metal oxides-based catalysts such as MnO_2 and CeO_2 [52,53]. The Hg(0) oxidation performance was recovered when SO_2 was lowered back to 200 ppmv, also indicating the competitive adsorption of SO_2 with HCl. XRD analysis for the spent catalyst can be used to identify possible sulfates formation [54]. As shown in Fig. 10, the XRD diffraction pattern was consistent with that for the fresh RuO_2 /rutile TiO_2 catalyst (Fig. 3), and the

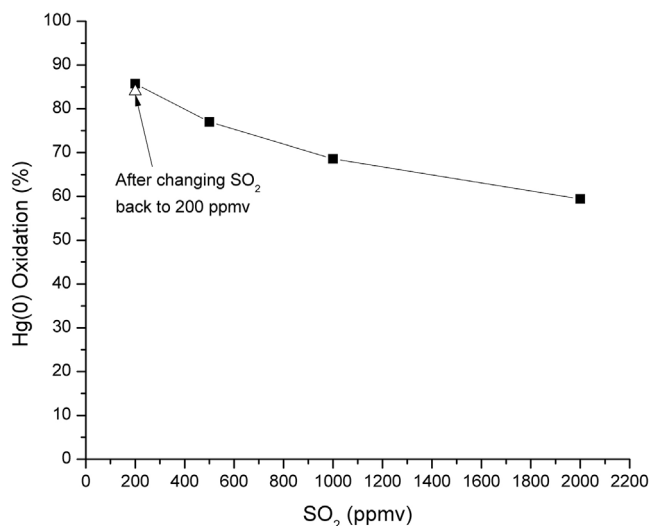


Fig. 9. Effect of SO₂ concentrations on Hg(0) oxidation performances of 1 wt% RuO₂/rutile TiO₂.WI catalyst under simulated flue gas. Conditions: 15 ppbv Hg(0), 10 ppmv HCl, 5 ppmv NH₃, 5 ppmv NO, 3%(v) O₂, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂ at 350 °C.

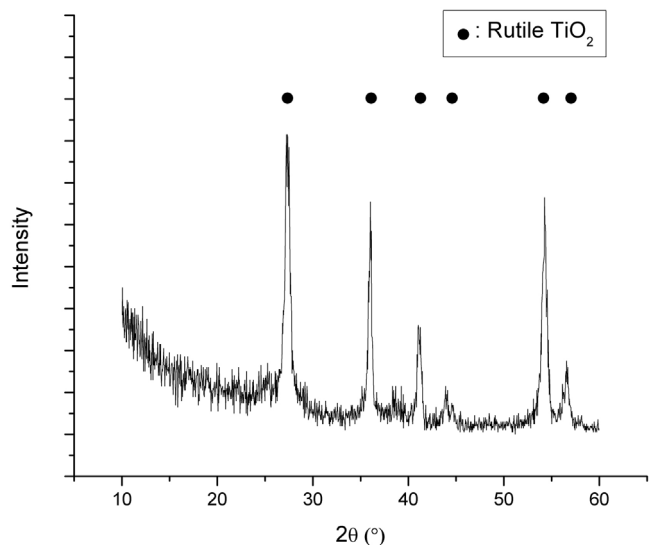


Fig. 10. XRD pattern of the spent RuO₂/rutile TiO₂ catalyst. Conditions: 15 ppbv Hg(0), 10 ppmv HCl, 5 ppmv NH₃, 5 ppmv NO, 200 ppmv SO₂, 3%(v) O₂, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂ at 350 °C for 48 h.

peaks for sulfate species were not observed. The XAFS analysis for the spent RuO₂/rutile TiO₂ catalyst (Fig. 4) did not detect a formation of any potential bonding between ruthenium and sulfur. These results indicated that the catalyst was not poisoned by SO₂ during the reaction. Other flue gas components such as CO₂, water vapor, and NO did not show any noticeable effect on Hg(0) oxidation over RuO₂/rutile TiO₂ catalyst.

The Hg(0) oxidation performances of RuO₂/rutile TiO₂ catalyst under simulated flue gas of sub-bituminous or lignite coal at the tail end of a SCR unit can be found in our previous paper [34]. The RuO₂/rutile TiO₂ catalyst showed better Hg(0) oxidation performances than the SCR catalyst under all HCl concentrations. With only 10 ppmv HCl, the oxidation was >85%, and >90% could be achieved at 25 ppmv HCl under a typical simulated flue gas condition of low rank coal. For the scenario of bromine addition, HBr is at least 10 times more effective than HCl and >90% Hg(0) oxidation performance could be achieved with <1 ppmv HBr. Again, the

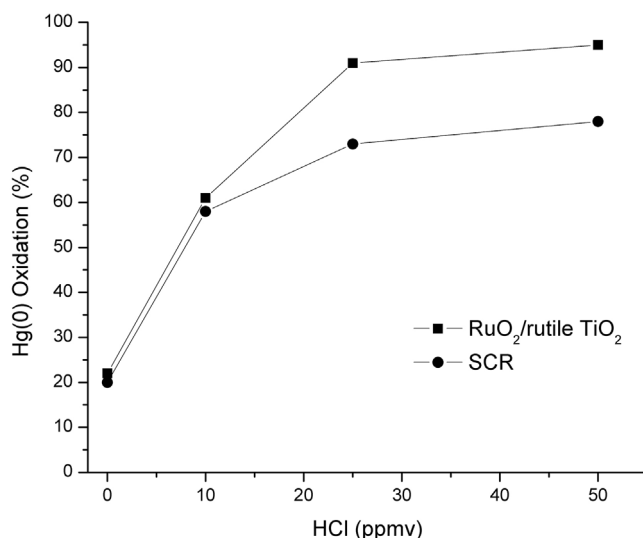


Fig. 11. Hg(0) oxidation performances of 1 wt% RuO₂/rutile TiO₂.WI catalyst with respect to different HCl concentration under a simulated flue gas condition of high sulfur bituminous coal. Conditions: 15 ppbv Hg(0), 5 ppmv NH₃, 5 ppmv NO, 2,000 ppmv SO₂, 3%(v) O₂, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂ at 350 °C.

RuO₂/rutile TiO₂ catalyst performed better than the SCR catalyst under all HBr concentrations.

Bituminous coal usually has high sulfur and chlorine contents with typical concentrations of ~1,000–2,000 ppmv SO₂ and ~50–200 ppmv HCl. Such high SO₂ concentrations usually significantly decrease the Hg(0) oxidation performances of most metal oxide-based catalysts [53,55,56]. The performance of the RuO₂/rutile TiO₂ catalyst with a simulated flue gas containing 2,000 ppmv SO₂ is shown in Fig. 11. Although the Hg(0) oxidation performance at low HCl concentrations (e.g. <10 ppmv) decreased, >90% Hg(0) oxidation performances were obtained at a typical HCl concentration range (e.g. >50 ppmv) of bituminous coal. Overall, the RuO₂/rutile TiO₂ catalyst has excellent Hg(0) oxidation performance and superior resistance to high SO₂. One drawback of typical vanadium-based SCR catalysts is that V₂O₅ can also oxidize SO₂ to SO₃. The SO₃/H₂SO₄ emissions can cause corrosion problems and plume opacity especially when high sulfur coals are used. Therefore, the vanadium loading on SCR catalysts is limited by SO₃ generation and typical commercial SCR catalysts try to keep the SO₂ conversion below 1% [50]. The conversion was measured for the RuO₂/rutile TiO₂ catalyst under the above simulated flue gas containing 2,000 ppmv SO₂. It was found that only 0.17% of the SO₂ was oxidized to SO₃, demonstrating another advantage of the RuO₂/rutile TiO₂ catalyst under high sulfur conditions.

In our previous study, oxidized mercury species obtained from the RuO₂/rutile TiO₂ catalyst were analyzed using XAFS [34]. In the presence of HCl or HBr gas, HgCl₂ or HgBr₂ was found to be the major oxidized mercury species. HgCl₂ and HgBr₂ have high solubility in water, and can be easily scrubbed by wet FGD scrubbers in coal-fired power plants.

4. Conclusions

In this study, the RuO₂/rutile TiO₂ catalyst for Hg(0) vapor oxidation was systematically studied in terms of different TiO₂ phases and synthesis methods for the first time. A combination of the two structurally similar components of RuO₂ as the active component and rutile TiO₂ as the support resulted in excellent RuO₂ dispersion over the rutile TiO₂ phase as opposed to anatase TiO₂ and thus high catalytic activity. The RuO₂ catalyst supported on rutile TiO₂ showed much higher Hg(0) oxidation activity than that on

anatase TiO₂. Among 0.2, 0.5, and 1 wt% Ru loadings, 0.5 wt% Ru loading onto rutile TiO₂ gave the highest turnover frequency for Hg(0) oxidation. Different synthesis methods (WI, DP and SEA) did not show noticeable differences in the morphology or the activity of the RuO₂/rutile TiO₂ catalyst. The RuO₂/rutile TiO₂ catalyst performed well in a typical SCR temperature window of 350–400 °C and preferred higher temperature. NH₃ and SO₂ gases had negative effects on Hg(0) oxidation performances due to competitive adsorption with HCl. Between the two gases, the RuO₂/rutile TiO₂ catalyst was more prone to NH₃. However, the catalyst showed very good Hg(0) oxidation performances under typical simulated flue gas conditions of sub-bituminous and lignite coals with low concentrations of HCl or HBr. It also showed excellent resistance to SO₂ in comparison with a SCR catalyst under typical simulated flue gas conditions of high sulfur bituminous coal with up to 2,000 ppmv SO₂. It has potential for Hg(0) oxidation at the tail end section of the SCR unit in coal-fired power plants especially for high sulfur conditions where the catalytic activities of most metal oxide- or noble metal-based catalysts are significantly inhibited.

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